INTERACTION BETWEEN AMORPHOUS SEMICONDUCTOR THIN FILM AND ELECTRON BEAM

Arthur C. M. Chen

General Electric Corporate Research and Development

Prepared for:

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Army Research Office-Durham

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Arthur C. M. Chen

General Electric Corporate Research and Development
Schenectady, New York
Telephone: AC518-346-8771

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TECHNICAL SUMMARY

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A research effort to understand electron beam enhanced crystallization process in amorphous semiconductor thin film has been initiated. Some preliminary results on light effect on crystallization temperature are reported here.

Finally, we have investigated the process and thickness dependence of crystallization temperature, T_x, in Ge-Te-As thin films. There is an increase in T_x for film thicknesses of less than 0.7μ. This phenomenon is the result of the strong influence of the surface in the crystallization nucleation process in very thin film. In addition there is a "stabilization process" in the RF sputtering process of these thin films where the films deposited from virgin sputtering targets exhibited a Te deficiency. The cause of this phenomenon is probably due to the loss of Te during the sputtering target hot press preparation process.

The above process dependence of T_x in Ge-Te-As film has an implication on the problems of device fabrication and will be briefly discussed.

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INTERACTION BETWEEN AMORPHOUS SEMICONDUCTOR THIN FILM AND ELECTRON BEAM

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I. INTRODUCTION

This is the second semiannual technical report on the research program, Interaction Between Amorphous Semiconductor Thin Film and Electron Beam, sponsored by the U. S. Army Research Office, Durham, North Carolina and the Advanced Research Project Agency, Arlington, Va. under contract DAHC-04-72-C-0016. As the research sponsorship will be continued, this report describes the progress and the results of the research program during the period Sept. 7, 1972 to May 7, 1973.

The objective of the program is to gain an increased understanding of the switching properties of amorphous semiconductor thin films by the use of electron beam as a diagnostic tool. As described in our first semiannual technical report on August 30, 1972, the research program scope had been enlarged to encompass a study of the possible device and system characteristics of an amorphous semiconductor electron beam memory because of the potential utility of the above devices in large computer system applications. The potential device and system characteristics of such memory device was reported in the first semi-annual technical report.

In our first year of research effort, we have developed a very good qualitative understanding of the possible device and system characteristics of the amorphous semiconductor electron beam memory. These characteristics and their performance limitations are based upon certain basic physical constraints of electron beam devices as well as upon the assumed or estimated parameters of electron beam-amorphous semiconductor thin film interactions. During the second half of the above contract period, we embarked on a program to understand further and to measure quantitatively the electron beam-amorphous semiconductor thin film interaction parameters. The quantitative determination and the theoretical understanding of these physical phenomenon will enable us to evaluate more accurately the possible device and system characteristics of amorphous semiconductor electron beam memory as well as to work towards the realization of such a memory.

The first phase of this investigation is to determine the possible readout sensitivity or the modulation efficiency of amorphous semiconductor thin films as an electron beam memory medium. The preliminary research effort of this phase will be reported in the publication, "Readout Sensitivity of An Amorphous Semiconductor Electron Beam Memory," Journal of Applied Physics, April 1973. We have continued this investigation to other Ge-Te-As systems. Some results of this investigation will be described in this report.

The second phase of this investigation is to determine the writing speed of the "recording sensitivity" of amorphous semiconductor thin film to electron beam excitation. The recording process appears to be a manifestation of electron beam enhanced crystallization phenomenon in amorphous semiconductor thin films. We have initiated an investigation of this phenomenon, and some preliminary results will be reported.

Finally, as a part of our research effort we have been studying the deposition process of amorphous semiconductor thin film in order to fabricate reproducible samples and to study possible influences of process variation on the interaction between amorphous semiconductor thin films and electron beam. In the course of our investigations we have elucidated two process parameters which change the crystallization temperature of the films and thus affect the behavior of amorphous semiconductor thin film not only in electron beam memory but also in other devices. One process parameter is the stabilization of the surface of the new sputtering target; the other is the thickness dependence of the crystallization temperature. This investigation is fairly complete and will be reported here.

II. ELECTRON BEAM READOUT SENSITIVITY OF AMORPHOUS SEMICONDUCTOR THIN FILMS

As described in the introduction, we are continuing our investigation of the electron beam readout sensitivity of amorphous semiconductor thin films to determine the suitability of these films for electron beam memory storage targets. The readout sensitivity of the thin film storage target can be described by

$$S = (\delta' - \delta^0)/\delta^0 \tag{1}$$

$$= [(\delta_c - \delta_a)/\delta_a] + [(\delta_\theta - \delta_0)/\delta_0] \tag{2}$$

$$= [(\delta_c - \delta_a)/\delta_a] + \exp\ [k(1 - \cos\theta)] - 1 \tag{3}$$

The first term of the above equation describes the effect due to the difference in the secondary yield between the amorphous and the crystalline phases; the secondary term describes the effect of surface deformation which occurred during the phase transition. δ_c and δ_0 are the yields of oblique and normal incident electrons impinging upon the crystalline phase. θ is the angle of surface deformation and k is the secondary electron angular coefficient whose detailed derivation is given in the first semi-annual technical report.

The high vacuum apparatus for measuring the angular dependence of the secondary yields of these films described in the first semi-annual technical report was used to continue our investigation. The film was $Ge_{15}Te_{81}As_4$. This film composition was examined as it is near the Ge-Te eutectic and is similar to the composition used used in read most memory devices. Thus this composition may be a possible erasable memory target for electron beam memory.

Thin amorphous films of $Ge_{15}Te_{81}As_4$ were prepared by RF sputtering. The film thickness was approximately 5000Å thick. In contrast to our earlier work in which we have used films prepared from hot pressed sputtering targets, these films were prepared from commercially purchased targets from Energy Conversion Devices, Inc., Troy, Michigan. Microprobe analysis verified the desired composition of these films.

The secondary electron yields of the amorphous and the crystalline phase with normal incident electrons are shown in Fig. 1. The yield of the amorphous phase of $Ge_{15}Te_{81}As_4$ are similar to those of other Ge-Te-As films we have reported. However, the most striking difference between $Ge_{15}Te_{81}As_4$ and the others, $Ge_{4.8}Te_{78}As_{17.2}$, $Ge_{37}Te_{60}As_3$ and $Ge_{39.4}Te_{60.3}As_{0.3}$ is that in contrast to the other films, the yield of the crystallline phase is higher than that of the amorphous phase. Thus in a scanning microscope, the crystalline phase would appear to be darker than the amorphous phase if secondary electron detection is used. In addition the difference in yield between the amorphous and the crystalline phase is a large and constant value. At 5 kv, S due to measured

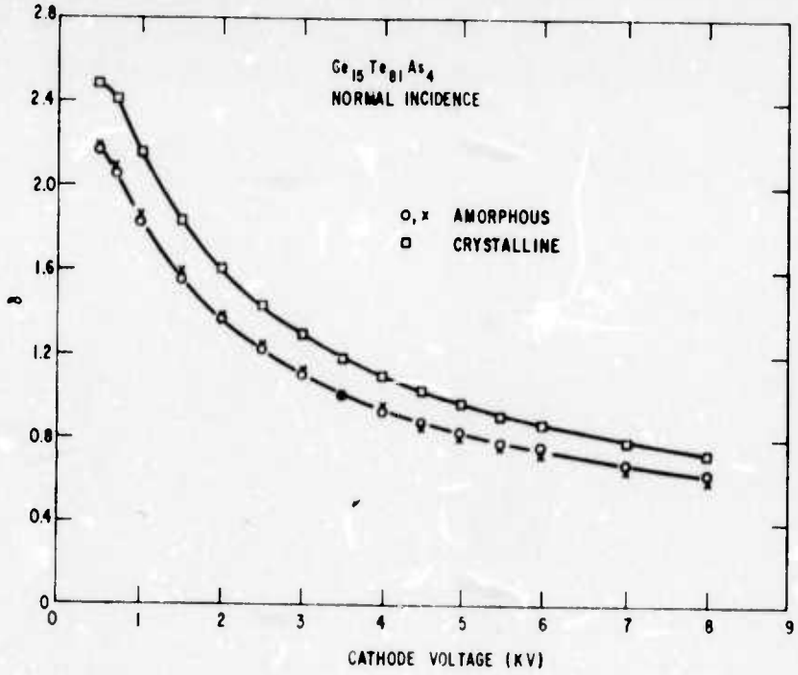

Figure 1 Secondary electron yield of amorphous and crystalline phases of $Ge_{15}Te_{81}As_4$. Normal incident electrons.

difference in yield would be 0.2, a very reasonable value of readout sensitivity for practical electron beam memory applications.

The possible electron beam readout sensitivity for $Ge_{15}Te_{81}As_4$ due to surface deformation was determined by measuring k, the angular coefficient. k for both the amorphous and the crystalline phase of $Ge_{15}Te_{81}As_4$ are shown in Fig. 2. The value and the voltage dependence of k are very similar to those of $Ge_{37}Te_{60}As_3$ reported in the first semi-annual report. The possible readout sensitivity or modulation efficiency with the above k values are also described in the above report.

The reversal in the change of the secondary yield between the amorphous and the crystalline phases of $Ge_{15}Te_{81}As_4$ was a surprise. It would appear that films of various chalcogenide composition may exhibit many differences in their electron beam readout sensitivity. For the above reason we are planning to continue our research in this area by examining the electron beam readout sensitivity of other chalcogenide thin films.

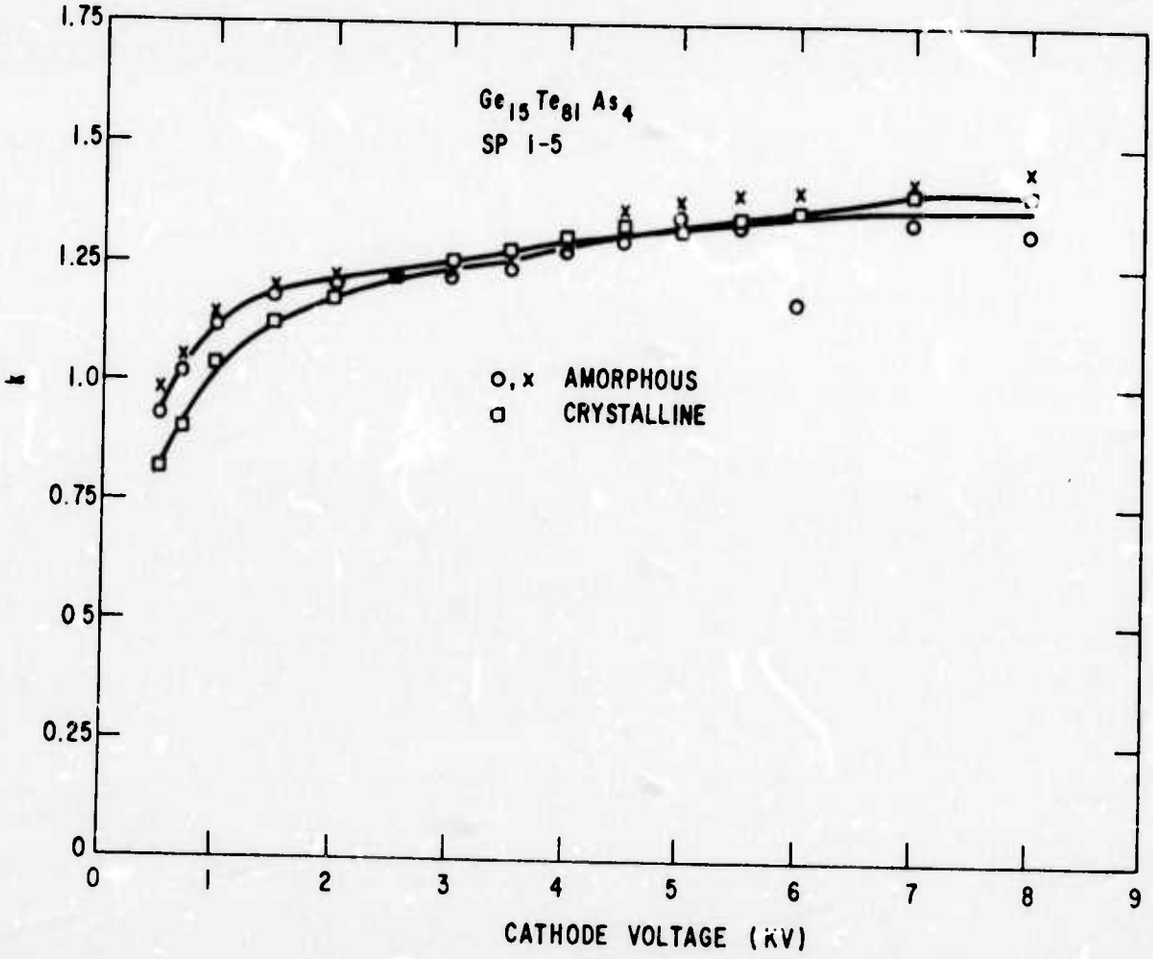

Figure 2 The secondary electron angular coefficient, k, of $Ge_{15}Te_{81}As_4$ thin film.

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III. ELECTRON BEAM ENHANCED CRYSTALLIZATION PROCESS IN AMORPHOUS SEMICONDUCTORS

Our investigations have shown that amorphous semiconductors can be crystallized with a high energy electron beam with an exposure time of 50 ns. Lower energy electron beams have induced crystallization in less than 10 μs. These fast rates suggested strongly that the crystallization process in amorphous semiconducotrs is enhanced by the electron beam.

Photon enhancement of the rate of crystallization in amorphous Se has been reported by Dresner and Stringfellow,[1] and are suspect to occur in other amorphous semiconductor thin films during laser writing processes. More recnetly Hamada et al. have studied the transient phenomenon associated with photocrystallization process in amorphous semiconductor films. They have shown that crystallization is completed within 50 μs..[2]

A qualitative indication of rapid electron beam enhanced crystallization process has already been suggested by our preliminary investigation. Our research goal is to understand the physical nature of this process. That is, we need to have good quantitative measurements of this phenomenon in order to be able to develop some theoretical understanding.

A possible method of investigation utilizes the crystallization temperature, T_X, of these thin films as a probe to measure the influence of photon and electron beams on the crystallization process. In essence, we want to determine the change,. if any, in T_X as a function of the incident flux and energy. As the masses of the thin films samples are too small for normal DTA analysis we have used resistance vs temperature as the tool for measuring T_X. We have verified the results of Messier and Roy,[3] that this technique is repeatable in measuring T_X to within ±1. 5°C.

The electronic apparatus for this measurement with photon excitation is described in Section IV A. Similar electronics will be used for electron beam excitation. We have conducted some preliminary experimentation with both RF sputtered and flash evaporated samples using the above appratus with an ordinary microscope light as the light source. The results are summarized in the following table.

All the flash evaporated samples of Ge-Te-As system showed large photoconductivity and exhibited a decrease in T_X with illumination. A very encouraging result. The RF sputtered showed little or no photoconductivity and some exhibited no change in T_X with illumination. Sample SP 1975-1, $Ge_{15}Te_8Sb_4$, did not have a well defined T_X. The change in resistivity occurred over a range of 20°C. Still it exhibited no change in T_X with illumination.

The preliminary results do suggest that T_X can be used as a probe in determining the photon or the electron crystallization process. To obtain more

Effect of Light on T_X (°C)

RF Sputtered Samples	T_X (dark)	T_X (light)	ΔT_X
SP 544006-5	243.5	238.6	4.9
SP 336007-11	243.5	243.5	---
SP 336007-9	192.2	192	---
SP 1975-1	198-221	197-222	---
Flash Evaporated Samples			
EV 51	246	233	13
EV 44	169	158	11
EV 43	254	248.5	2.2
EV 39	152-160	137-147	5-23
EV 36	186	179.5	6.5

precise quantitative and thus more meaningful results with electron beam excitation we are changing and improving our electron beam test cell.

The improvements needed are in better electron-optics and electron source for higher intensity beam with a small spot size, high vacuum heated sample stage and a precise temperature controller to control the temperature of this sample stage. Unfortunately, these improvements are major undertakings and will take time and effort to complete. They were begun at about January 1973, and will take at least seven months for completion.

IV. PROCESS AND THICKNESS DEPENDENCE OF CRYSTALLIZATION TEMPERATURE OF Ge-Te-As AMORPHOUS THIN FILMS

In our computer simulation of the electron beam heating process in amorphous semiconductor thin films,[4] it became very evident that film thickness was a crucial parameter which affected the heating process. The electron beam at a given voltage had a certain penetration range and dissipated most of its energy within this region. As amorphous semiconductors have very low thermal conductivity (~1/10 that of glass), the thermal boundary conditions were strongly dependent on the relative film thickness compared to the electron range. If the film thicknesses were less than the electron range, the film substrate interface would behave almost as an isothermal wall because the bulk substrate (Si) would act as a heat sink and maintain the interface near to ambient temperature. If the film thicknesses were more than twice the electron range, then the amorphous semiconductor would act as an adiabatic wall and retain all the dissipated electron beam energy to heat the material. The efficiency of the electron beam heating process is intimately tied to the film thickness.

In addition to the above relatively obvious connection between thickness and beam heating efficiency, the work of Takamori, Messier and Roy on "explosive crystallization "[5] in amorphous germanium stimulated certain speculation on our part. This explosive crystallization phenomenon appears only in film with greater than 10μ thickness. Such "thick" thin films must have a great deal of internal stress, and the explosive crystallization appears to be a dramatic manifestation of a possible strain induced crystallization phenomenon.

If internal strain may influence the crystallization process, subtle but significant changes in crystallization behavior may be observed in thinner amorphous semiconductor thin films. In particular, the crystallization temperature of these films may be a function of film thickness.

The above two factors; the importance of film thickness in electron beam heating and thus in the recording process and the possibility of additional complications of a change in crystallization temperature with film thickness prompt us to initiate a study on the thickness dependence of crystallization temperature in amorphous semiconductor thin films.

A. TECHNIQUE AND APPARATUS

To study the possible subtle influences of thickness or other excitations on the crystallization temperature, T_x, of amorphous semiconductor thin films requires precise experimental tools. Because the masses of the thin film samples are too small for normal DTA analysis we have used the large change in resistance at the crystallization temperature as the tool for measuring T_x. This technique is highly reproducible;[3] and in our apparatus can repeatedly

determine T_x for selected samples to within ±1.5°C. By selected samples we mean that the thin film must exhibit a sharp amorphous to crystalline transition. For our particular study we have used thin films with nominal composition $Ge_{37}Te_{60}As_3$ which has the sharp phase transition characteristics and is a possible storage medium for archival electron beam memory. Amorphous films of $Ge_{37}Te_{60}As_3$ (0.05-10μ thick) were prepared by RF sputtering onto oxidized Si substrates. The electrodes were thin films Mo or Al.

The schematic of the resistance vs temperature measuring apparatus is shown in Fig. 3. The sample chamber is shown in Fig. 4. By the use of log amplifier to display the change in resistance vs temperature on a x-y recorder many samples may be quickly evaluated. The sample chamber consisted of a large Ni plated copper heated stage isolated from the other portions of the chamber by thin wall stainless tubing. The chamber itself can have inert atmosphere, N_2 or can be evaluated to a pressure of less than 2μ. Because of the good thermal isolation, we can obtain stable constant heating rates. An example of the heating rate is shown in Fig. 5. All measurements were usually made at a heating rate of 40°C/min. To maintain good thermal contact between the thin film sample and the heated stage, liquid Ga was used as the thermal contact. Thus the temperature difference between the sample and the heated stage was maintained at a constant of less than 3°C.

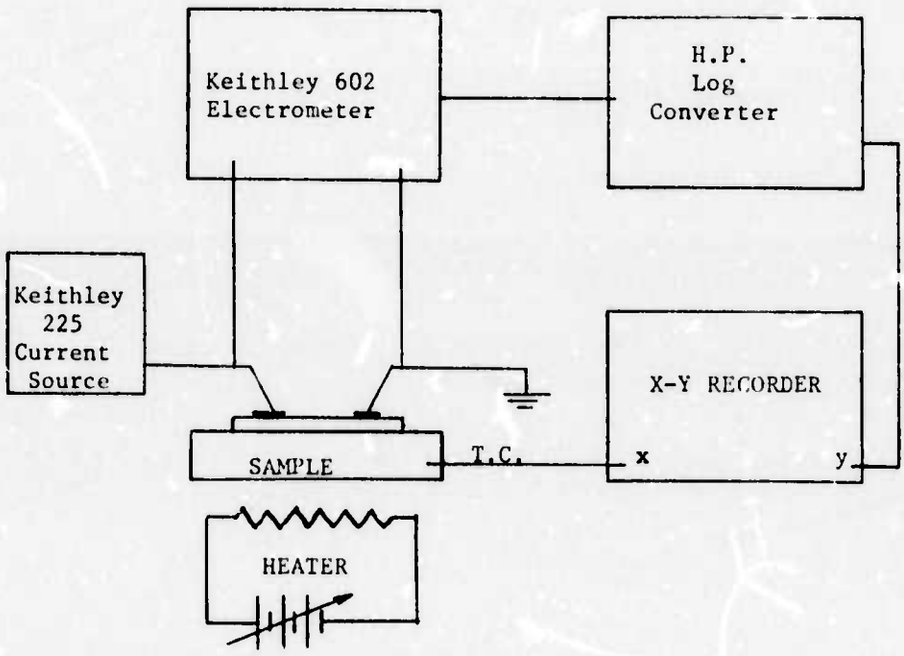


Figure 3 Thin film resistance vs temperature measuring apparatus.

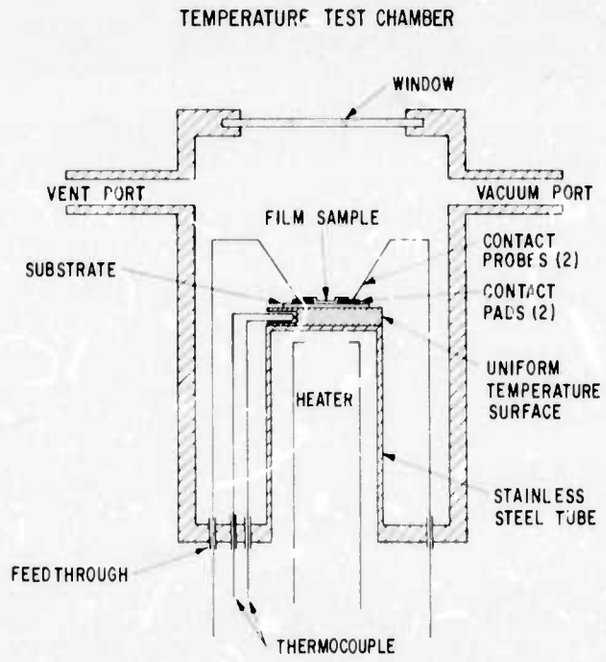


Figure 4 Sample chamber for measuring thin film resistance vs temperature.

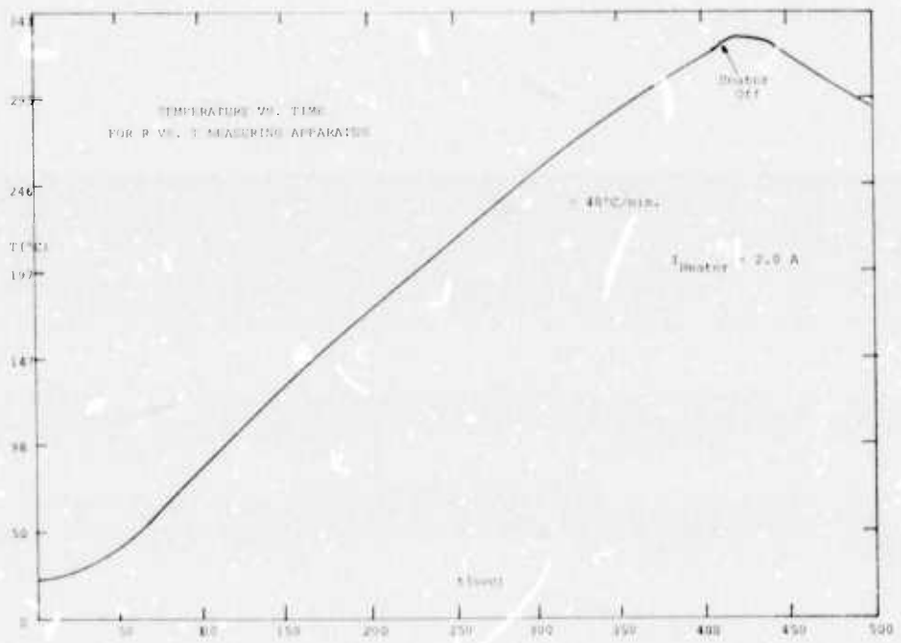


Figure 5 Constant heating rate of sample chamber vs time for the resistance vs temperature measuring apparatus. I_{heater} = 2.0A, rate = 44°C/min.

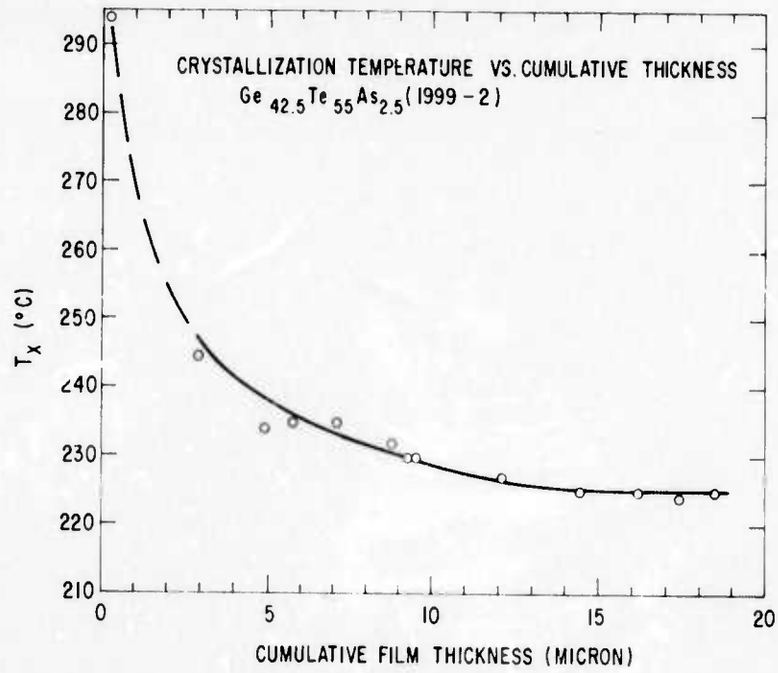


Figure 6 Change in T_X vs cummulative deposited film thickness for RF sputtering deposition from a "virgin" target of $Ge_{42.5}Te_{55}As_{2.5}$.

B. STABILIZATION OF THE SPUTTERING TARGET SURFACE

Our initial research results on thickness dependence of T_X were confusing. Although there were indications of a decrease in T_X of approximately 10-15°C with an increase in film thickness from 0.1 to 1.0μ, the results were not easily predicatable. The problem was traced to the need to stabilize the sputtering target or cathode. In our desire to do a careful investigation we had used a freshly prepared target. However there appeared to be a stabilization process which a new amorphous semiconductor sputtering target must undergo before the prepared films are reproducible. Once the sputtering target has stabilized by having deposited a cumulative film thickness of greater than 15μ, the the amorphous semiconductor thin films are reproducible in composition and T_X. In the experiments to be described, the sputtering target consisted of a hot pressed (≈0.100" thick) amorphous semiconductor glass on an aluminum plate. It was water cooled. The target diameter was 3.5" with the target-substrate distance of 3".

In general, RF sputtering process has produced thin multicomponent films which have the same composition as that of the cathode or the sputtering target. However, with a "virgin" multicomponent target, the component with a higher sputtering yield than the other components will come off faster during the very first sputtering process. An altered layer is soon formed such that there is a compensating deficiency in the higher yield component to result in a deposited film with composition very close to that of the target.

Prior experimental and theoretical studies with multicomponent metallic sputtering targets indicated that this stabilization process occurred very quickly ($<$1.0 sec.) and that the altered surface layer is very shallow ($<$200Å).

In preparing amorphous semiconductor thin films by RF sputtering, a similar phenomenon but with a dramatic different magnitude, was observed. The stabilization process which forms this altered layer is exhibited by the change in T_X as a function of the cumulative film thickness deposited from a "virgin" sputtering target of $Ge_{42.5}Te_{55}As_{2.5}$ (Fig. 6). The film thicknesses were all approximately 1.0μ deposited at a rate of 14 Å/sec. Neglecting the initial point, there is a decrease in T_X of ~20°C from the initial film until the cumulative film thickness has attained over ~15μ. T_X remained at 224 ± 1°C for cumulative thicknesses beyond 40μ.

This large change in T_X can be attributed to a variation in the composition of the deposited film during this stabilization period. The compositions of the above films were determined by microprobe analysis and the results vs the cumulative thickness are shown in Fig. 7. Except for the initial point, the films that were deposited first have higher Ge content; and resulted in a higher T_X. For comparison purposes, the dependence of T_X vs cumulative thickness is also shown in Fig. 7. The As content of these films is small and fluctuates about a small constant value of 2.5%. The higher Tx for the low cummulative film thickness is the result of higher Ge concentration is rather evident and collaborates well with the results reported by M. Sugi, et al.[6]

What are the possible causes of this stabilization process? We had previously described the usual formation of the "altered layer" in metallic multicomponent sputtering process. In the case of amorphous semiconductor sputtering targets, the stabilization phenomenon observed by us occurred in orders of magnitudes longer time and thickness when compared to the process of forming the "altered layer" in metallic targets. In addition, microprobe analysis of the composition of the films deposited during this stabilization process showed results contrary to our expectation.

Te has a lower sublimation temperature than Ge, and thus the sputtering yield will be higher for Te than for Ge. The phenomenon of forming the "altered layer" would produce, initially, film composition with higher Te content than the bulk target because of the higher Te yield. With subsequent

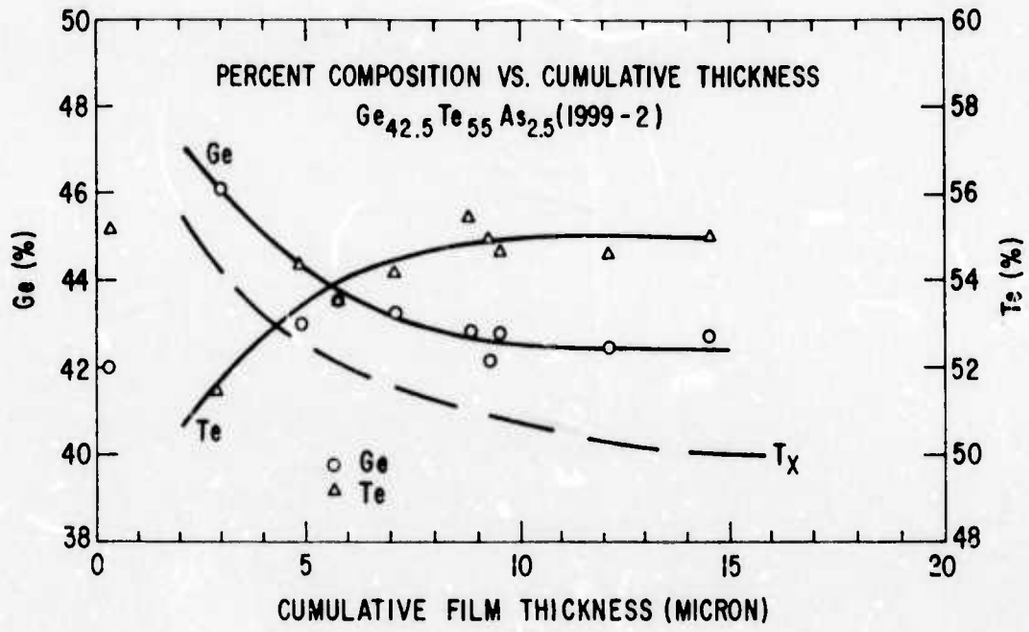


Figure 7 Film composition vs cumulative deposited film thickness for films in Fig. 6. T_X is shown for comparison.

sputtering the Te content would decrease as the "altered layer" would form with a higher Ge content to compensate for its lower sputtering yield. Our microprobe analysis gave the contrary results. (See Fig. 7). The initial films were Te deficient and with subsequent sputtering, the Te content increased until it attained the bulk value. These microprobe analysis results and the large time and thickness disparity between the normal formation of the "altered layer" and the observed stabilization process in amorphous semiconductor sputtering targets forced us to look for another and a more reasonable explanation of this process.

One possible cause of this stabilization process is in the sputtering target preparation process itself rather than in the subsequent sputtering process. Our sputtering targets were prepared by hot pressing a very thin layer (~ 0.100") of powdered glass onto aluminum back plate. We have developed this process so that the target surface can be efficiently cooled to minimize or to eliminate possible thermal evaporation during the sputtering process. The hot pressing process takes place at about 15°C above the glass softening point. In hot pressing the target, it is inevitable that, initially, the pressing apparatus and thus the target surface will be hotter than the interior of the glass powder target. Because Te has a low sublimation temperature and thus high vapor pressure at the processing temperature, there may be a preferential loss of Te from the surface of the sputtering target. This loss in Te manifests itself as the measured Te deficiency in the initially deposited films from a

virgin sputtering target. If we assume that the RF sputtering depo ition process takes place with a 100% efficiency, then the loss of Te during the hot pressing target preparation takes place within 15-20μ of the target surface.

C. THICKNESS DEPENDENCE OF CRYSTALLIZATION TEMPERATURE

Once the sputtering target has been "stabilized," and thin film samples can be reproducibly prepared, we can study the thickness dependence of the crystallization temperature. Thin films of $Ge_{42.5}Te_{55}As_{2.5}$ with thicknesses of 0.1 to 1.5μ were prepared from "stabilized" sputtering targets. The deposition rate ranged from 4 to 20 Å/sec. Microprobe analysis shows these films to have essentially the same compositions. The crystallization temperatures of these films as a function of film thickness are shown in Fig. 8. Independent of the deposition rate, there is an obvious increase in T_X, of approximately 15°C for thicknesses below 0.7μ. Above 0.7μ, T_X remains at 224 ± 1°C. The distribution in T_X for thicknesses greater than 0.7μ probably is due to normal process and measurement variations.

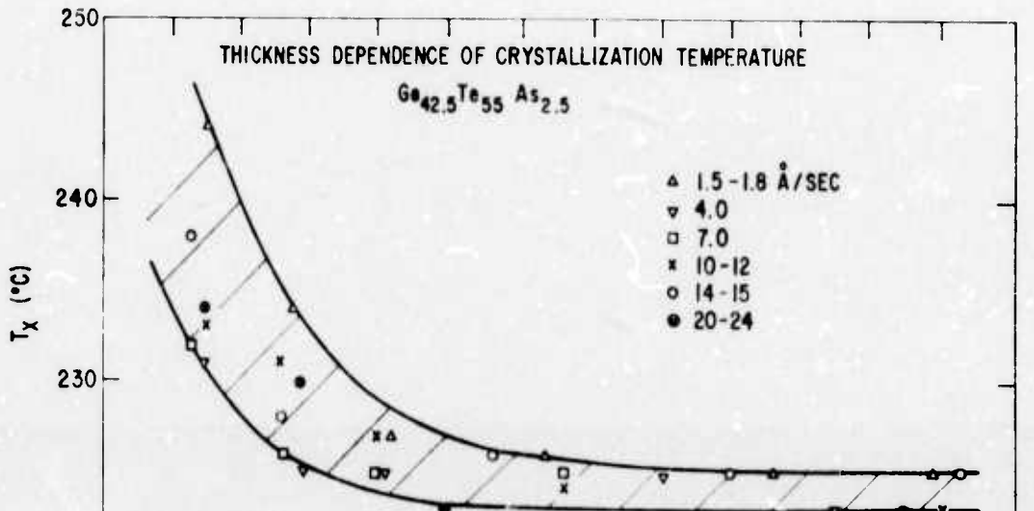


Figure 8 Change in T_X vs film thickness for $Ge_{42.5}Te_{55}As_{2.5}$ deposited at various rates.

The increase in T_X with decrease in film thickness indicates that higher energy is required to induce the amorphous to crystalline phase transition in

thinner films. The need for higher energy to induce other phase transition phenomenon (i.e., ferroelectric, ferromagnetic, etc.) in thin films has been observed in the past and has been attributed to the need to overcome higher surface energy in very thin films. Similar to other phase transformation nucleation phenomenon plays a dominant role in the amorphous to crystalline transition. The nucleation rate is generally described by I, where

$$I = w(\gamma)\, n(\gamma). \tag{4}$$

$w(\gamma)$ is the kinetic term which describes the process, such as diffusion, which enables nuclei of radius γ to form. $n(\gamma)$ is the equilibrium concentration of crystalline nuclei. It is in general given by

$$n(\gamma) = n_0\, e^{-\Delta G/kT} \tag{5}$$

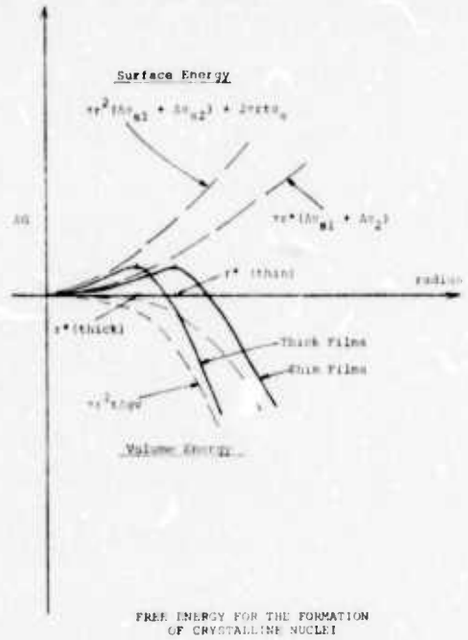
where ΔG is the difference in free energy between the crystalline and the amorphous phase.

If we consider a simple model of cylindrical nuclei with height of the film thickness, t, then

$$\Delta G = \pi\gamma^2 (\Delta\sigma_{s1} + \Delta\sigma_{s2}) + 2\pi\gamma t\sigma_s + \pi\gamma^2 t\Delta g_v \tag{6}$$

The first two terms are the surface energy and the last term is the volume energy of the nuclei respectively. σ_{s1} and σ_{s2} referred to the two surfaces of the film. σ_s and Δg_v are the surface energy and the volume free energy of the crystalline phase respectively. The nuclei are stable if it is greater than r*, the critical radius. It is derived by solving the equation $\partial\Delta G/\partial\gamma = 0$. The effect of thin and thick films can be pictorially described by referring to Fig. 9.

For thin films, the surface energy will be dominated by $\pi\gamma^2(\Delta\sigma_{s1} + \Delta\sigma_{s2})$ if we assume $t << r$ as the criterion for the thin films and $\Delta\sigma_{s1} \simeq \Delta\sigma_{s2} \simeq \sigma_s$. For thicker films where $t > r$, then both surface energy terms will come into play. Again because of the larger t, thicker films will have a larger volumetric free energy. The above factor combines to make the critical radius, r*, smaller for thicker films than for thinner films as pictorially shown in Fig. 9. As the critical radius r* is larger for thin films, the amount of atomic diffusion required to form the stable nuclei are larger. These two factors combined to determine a higher crystallization temperature for the thinner films.



FREE ENERGY FOR THE FORMATION
OF CRYSTALLINE NUCLEI

Figure 9 The difference in free energy, ΔG, for crystalline nuclei formation for thin and thick amorphous semiconductor thin films.

D. IMPLICATIONS AND CONCLUSIONS

Our rationale to study the thickness dependence of crystallization temperature was because of the possible importance of this phenomenon to electron beam memory. In addition our study led us to the discovery of a stabilization process in the preparation of these thin films by RF sputtering. What have we learned from this study?

First of all, amorphous semiconductor thin films are not necessarily immune to the need for careful process control if the goal is to make reproducible films for devices or for the study of its physics. The stabilization process shows that one does not necessarily produce films with the same composition as that of the sputtering target, if one is not careful. The thickness dependence of the crystallization temperature shows that even with a reproducible process there are fundamental physical phenomena which may affect T_X and thus affect memory device behavior.

Our investigation has shown that for $Ge_{42.5}Te_{55}As_{2.5}$ the crystallization temperature stabilized to a constant value for thickness greater than 0.7μ. A possible physical basis for the increase in T_X for thickness less than 0.7μ is the influence of surface energy on the crystallization phenomenon. If this is true then similar phenomena would be expected to occur in other Ge-Te-As

thin films and in devices which depend on amorphous to crystalline phase transition as its functional mechanism. To assure reproducibility and high yield in these devices, it would be highly desirable to make the amorphous semiconductor thin films greater than 1μ thick to eliminate the possible change in T_x due to thickness in these devices.

V. PARTICIPATING TECHNICAL PERSONNEL

A. C. M. Chen

A. M. Dunham

J. M. Wang

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